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COMPLETE SPECIFICATION

Detergent Compositions

We, COLGATE-PALMOLIVE COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 300 Park Avenue, New York 22, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to detergent compositions suitable for washing household linens.

These compositions comprise at least one detergent (soap or a synthetic detergent) and usually also contain inorganic salts which or may not be detergent adjuvants (principally alkaline phosphates), and possibly other ingredients such as anti-redeposition agents, optical bleaching agents, perfumes and anti-corrosion agents.

It has long been recognised that such detergent compositions do not always suffice to remove stains from cloth under normai washing conditions, for some stains are marks caused by various colouring matters which are fixed on the textile fibres by a mechanism analogous to dyeing. Such colouring matters are very common and are found, for example, in wine, tea, coffee, cocoa, fruits and lipstick.

To eliminate these colouring matters it is generally necessary to resort to an oxidising treatment. That is why a large number of detergent compositions contain, as well as the constituents mentioned above, a certain amount of a per-salt, the most common being sodium perborate, most usually in amounts between 5 and 30% by weight of the total composition.

It is with detergent compositions containing a water-soluble perborate that the invention is concerned, the aim of the invention being to improve the bleaching effect of the perborate.

Not all the perborate in such compositions is used effectively for oxidising colouring matters. To be effective it must take part in an oxidation reaction which bleaches the colouring matter, but some of it decomposes into borate and gaseous oxygen. This evolution of gaseous oxygen, which plays no part in oxidising the colouring matters, represents a total loss of a significant amount of the perborate, which is an expensive material.

It is well-known that heavy metals, present as impurities in the washing water or washing vessels, catalyse the decomposition of perborate. It has therefore been suggested, in order to stabilise the perborate, to add to detergent compositions powerful sequestrating agents such as ethylene diamine tetraacetic acid (EDTA) or its salts, or diethylene triamine pentaacetic acid (DTPA) or its salts. It has now been found that the presence of such sequestrating agents, while effectively improving the stability of the perborate, greatly interferes with its bleaching power.

It is also known that water-soluble copper salts have an activating effect on the bleaching power of the perborate in a detergent composition used at moderate temperature (40 to 60° C.), but it has been found that if such a composition is used at the boil, the copper salts cause such rapid decomposition of the perborate that the bleaching power is considerably reduced, unless the concentration of copper is precisely controlled and extremely small (0.1 to 1 p.p.m), which is in the region of the amount of metal present as an impurity in washing solutions.

The present invention is based upon the above two findings and the further discovery that in the presence of a powerful sequestrating agent increasing amounts of a copper salt first greatly increase the bleaching power, and then above a certain concentration greatly decrease it. Thus there exists an optimum concentration of copper ions, above which the rate of decomposition of the perborate, increasing with the concentration of copper

ions, becomes too rapid for good bleaching (10^{-3} to 10^{-4}M).

If the copper ion concentration is slightly outside the optimum, which is in the neighbourhood of 10^{-6} to 10^{-5}M., there is a definite falling off in the bleaching effect. However, it would seem almost impossible in practice to maintain this optimum concentration because of the very small amounts involved and the variable amounts present in the water, the cloth and the washing vessels. The present invention provides a solution to this problem.

According to the invention, a stable, substantially dry perborate-containing detergent composition comprises a water-soluble anionic or non-ionic organic detergent (e.g. a sodium salt of an alkyl benzene sulphonic acid containing from 10 to 16 carbon atoms in the alkyl group), a water-soluble perborate, a water-soluble copper salt, and a sequestering agent stable in the presence of the perborate and which forms with copper a complex having a dissociation constant the common logarithm of which is between -11 and -15, the copper salt and the sequestering agent being present in amounts sufficient to enhance the bleaching action of the perborate at the boil.

The many known sequestrating agents, which have the property of forming complexes with metal ions, are distinguishable by the stability of the complexes they form with various metals. These complexes are always partially dissociated, that is, they are in equilibrium with free metal ions, the quantity of free ions being lower, the lower the dissociation constant of the complex. Considering the equilibrium system set up between a soluble metal salt and an excess of sequestrating agent, the free metal ion concentration is relatively independent of the total amount of salt present and substantially dependent on the dissociation constant of the particular complex, so that a metallic buffering effect is exerted.

Thus a combination of sequestrating agent and copper salt may be chosen such that in a perborate-containing detergent composition the bleaching efficiency of the per-salt may be maintained at substantially optimum level over a wide range of concentration of the copper salt.

As already indicated, sequestrating agents which are suitable for use in the perborate-containing detergent compositions of the invention are those wherein the dissociation constant of the copper complex is between 10^{-11} and 10^{-15}, i.e. the common logarithm of the dissociation constant is between -11 and -15.

The dissociation constants are those calculated under the usual conditions given in the literature, that is: temperature—20 to 30° C., ionic strength – 0.1, electrolyte—KCl.

Although the conditions encountered during washing operations are not identical with those above, nevertheless the dissociation constants calculated under those conditions are convenient in choosing an appropriate sequestrating agent for use in the detergent compositions of the invention.

Among the sequestrating agents which satisfy those conditions are the following, the dissociation constants being given in logarithmic form:

	Dissociation constant of the cupric complex (log)
Methylaminodiacetic acid	11.09
Aminotriacetic acid (ATA)	12.68
Hydroxyethylaminodiacetic acid	11.90

Of these sequestrating agents, aminotriacetic acid (ATA) is preferred.

Leucine and asparagine have suitable dissociation constants, but are not sufficiently resistant to oxidation in the presence of perborate.

Usually the amount of copper salt is such that the detergent composition contains 30 to 300 p.p.m. (parts per per million) by weight of copper, preferably 40 to 80 p.p.m., and the amount of sequestrating agent is such that 3 to 15, preferably 10 to 13, molecules of sequestrating agent are present for every atom of copper in the composition.

The experimental results on which the invention is based are described below. In the examples, the percentage bleaching efficiency (BE%) of the compositions tested was determined as follows:—

Samples of cotton fabric were dyed with a Ciba dyestuff known as "Noir pyrogene" and washed free of excess dye in the absence of any oxidising agent. These dyed samples, having a reflectance of the order of 20, were then washed in a glass beaker under specified conditions of temperature and duration of treatment with a composition containing a perborate. The perborate partially oxidised

the dyestuff, and the sample, after washing, was lighter in colour. The reflectance of the samples was measured using a Hunter photocolorimeter fitted with a green filter. If the reflectance of the sample before dyeing is R_0, after dyeing and before washing is R_1, and after washing is R_2, the bleaching efficiency BE is calculated by means of the formula:

$$BE\% = \frac{R_2 - R_1}{R_0 - R_1} \times 100$$

EXAMPLE I

This example illustrates the effect of adding copper only to a washing solution containing 12.5 g./litre of a perborate-containing detergent composition, when washing is performed at 60° C. and at 100° C.

The detergent composition used consisted of:—

Sodium dodecylbenzene sulphonate	—22%
Sodium tripolyphosphate	—30%
Fatty acid ethanolamide	—2.5%
Sodium silicate	— 7%
Magnesium silicate	— 1%
Hydrated sodium perborate	— 10%
Various additives, such as colouring matter, perfume, sodium sulphate and moisture	—as desired.

Table 1 summarises the results obtained.

TABLE 1

Amount of Cu^{++} present in the washing solution (in p.p.m.)	% Bleaching Efficiency	
	Washing 1 hr. at 60° C.	Washing 1 hr. at 100° C.
0	12.1	58.6
0.5	—	46.7
1.0	18.1	33.8
1.5	—	31.7
2.0	—	28.6
2.5	24.7	—
5.0	30.8	—
10.0	26.2	—
20.0	14.7	—

These results clearly indicate that the addition of copper, although improving the bleaching efficiency of the perborate at 60° C., is disadvantageous when operating at the boil (100° C.).

EXAMPLE II

This was carried out as in Example I, but at 100° C. only, and with 0.2% of a powerful sequestrating agent, EDTA, added to the detergent composition.

Table II shows the results obtained.

TABLE II

Amount of Cu^{++} present in the washing solution (in p.p.m.)	% Bleaching Efficiency
	Washing 1 hr. at 100° C.
0	37
0.5	45
1.0	59
2.5	65
5.0	58
10.0	38

This table shows that the bleaching efficiency first increases and then decreases as the amount of copper present is increased. There is thus an optimum concentration of copper which it is impossible to maintain in practice because of the the copper present as an impurity in the washing solution.

EXAMPLE III

This example shows that by using certain specific sequestrating agents in accordance with the invention the bleaching efficiency may be maintained high over a wide range of copper concentration, although other sequestrants do not give this effect.

The experiment was carried out using the composition described in Example I at two different concentrations, namely 5g./1. and 12.5g./1.

Various sequestrating agents were added, one at a time to the said detergent composition at a concentration of 0.2%, based on the total weight of the composition. Each of the compositions was tested for bleaching effect, according to the method described above, in the presence of 0, 1, 2, 3, 4 and 5 p.p.m. of copper ions, added to the detergent solution in the form of copper sulphate. The results obtained are shown in Table III. This table gives the maximum bleaching efficiency attained for each of the compositions and also the length of the bleaching "plateau". This "plateau" is defined as the range of concentration of copper ions (in p.p.m. in the washing solution) over which the bleaching efficiency is not reduced below 10% of its maximum value. The table shows that those sequestrating agents having a dissociation constant for the cupric ion complex in the range 10^{-11} to 10^{-15} give much better bleaching and have a high stability with respect to variations in the copper ion concentration.

TABLE III

Sequestrating Agent	Dissociation constant of the cupric complex (−log)	5 g./l. detergent		12.5 g./l. detergent	
		Maximum bleaching efficiency %	Length of the bleaching "plateau"	Maximum bleaching efficiency %	Length of the bleaching "plateau"
None	—	39	0.5	51	0.75
Dihydroxyethylamino diacetic acid	8.1	46	1.0	—	—
Aminoacetic acid	8.6	44	0.8	66	1.3
Aminodiacetic acid	10.5	53	2.0	—	—
Ethylene diamine	10.5	55	1.75	67.5	>4.2
Methylaminodiacetic acid*	11.1	53	3.8	64.5	>5.0
Hydroxyethylamino* diacetic acid	11.9	53	3.8	73	>4.9
Aminotriacetic acid*	12.8	60	4.7	73	>4.6
Diethylene triamine	16.0	59	2.9	—	—
Ethylene diamine tetra-acetic acid	18.5	56	1.0	69.5	2.1

* Sequestrating agents within the scope of the invention.

EXAMPLE IV

This example demonstrates that as a result of the increased bleaching efficiency of the perborate in compositions according to the invention, the perborate content may be reduced below that of detergent compositions containing a powerful sequestrating agent (EDTA) without copper.

The basic detergent composition was the same as in the preceding Examples. To one portion of the basic composition was added 0.2% of EDTA, and to a second portion were added 0.4% of ATA and 0.02% of anhydrous copper sulphate. A third portion contained 0.4% of ATA and 0.02% of copper sulphate, but the perborate content was reduced from 10% to 6%. The bleaching powers of these three samples after boiling for one hour were as follows:

EDTA/10% of perborate	— 29%
ATA/Cu/10% of perborate	— 45%
ATA/Cu/6% of perborate	— 36%

This experiment was extended as follows: The practical efficiency of the detergent was evaluated by washing household linen and examining each washed article visually, the results of this examination being expressed arbitarily by a numerical code. The combined results of a dozen comparitive washings using two detergent compositions were interpreted statistically to see if one of the compositions was significantly better than the other.

The trials were conducted by boiling in a galvanised iron vessel.

A first series of tests compared detergent compositions containing EDTA as the sequestrating agent in the absence of copper salt and with varying amounts of sodium perborate present. Under the test conditions, it was found that the perborate content could be reduced to 5% of the total composition with no apparent reduction in the bleaching effect compared with the standard composition containing 10% of perborate.

In a second series of tests the standard composition containing 10% perborate and 0.2% EDTA but no copper salt was compared with a composition containing 0.4% ATA and 0.02% of anhydrous copper sulphate and reduced amounts of sodium perborate. It was found that the amount of perborate could be reduced to 3% of the detergent composition without any significant difference in the bleaching effect compared with the standard composition containing 10% perborate.

Thus the invention provides perborate-containing detergent compositions having an increased bleaching efficiency compared with the usual compositions of the same perborate content, or compositions having the same bleaching efficiency as the usual compositions in spite of a reduced content of perborate.

Generally, compositions according to the invention may be formulated as follows:

Detergent (synthetic detergent, soap or mixtures of these)	4 to 40%
Adjuvant salts	40 to 90%
Perborate, particularly sodium perborate tetrahydrate	3 to 20%
Water-soluble copper salt in amount, based on the total composition, corresponding to	30 to 300 p.p.m. Cu
Sequestrating agent having a dissociation constant for the cupric ion complex of 10^{-11} to 10^{-15} per atom of Cu	3 to 15 molecules present.
Perfume, dye, blueing agent	0 to 1%

One of the possible methods of manufacture consists in spray-drying a mixture of the detergent, mineral salts and copper salt, and then adding to the dried product the perborate and sequestrating agent, as well as any other heat-sensitive constituent, such as perfume.

Other examples of compositions embodying the invention are as follows.

EXAMPLE V

Sodium tetrapropylenebenzene sulphonate	31%
Sodium tripolyphosphate	35%
Sodium silicate	5.8%
Sodium perborate (tetrahydrate)	10%
Other constituents, e.g. dye, perfume, sodium sulphate and moisture	as desired

EXAMPLE VI

Ethenoxylated tall oil (15 molecules ethylene oxide)	4%
Sodium tripolyphosphate	40%
Sodium silicate	7%
Sodium perborate (tetrahydrate)	10%
Other constituents, e.g. dye, perfume, sodium sulphate and moisture	as desired

EXAMPLE VII

Sodium dodecylbenzene sulphonate	8%
Sodium salt of sulphated fatty alcohol	8%
Fatty acid ethanolamide	3%
Sodium tripolyphosphate	40%
Sodium silicate	7%
Perborate	10%
Other constituents e.g. dye, perfume, sodium sulphate and moisture	as desired

EXAMPLE VIII

Sodium alkylaryl sulphonate	12%
Sodium salt of sulphated fatty alcohol	6%
Fatty acid ethanolamide	2.5%
Sodium tripolyphosphate	30%
Sodium silicate	7%
Magnesium silicate	1%
Perborate	10%
Other constituents e.g. dye, perfume, sodium sulphate and moisture	as desired

All parts and percentages are by weight unless otherwise specified.

WHAT WE CLAIM IS:—

1. A stable, substantially dry perborate-containing detergent composition which comprises, a water-soluble anionic or non-ionic organic detergent, a water-soluble perborate, a water-soluble copper salt, and a sequestering agent stable in the presence of the perborate and which forms with copper a complex having a dissociation constant the common logarithm of which is between -11 and -15, the copper salt and the sequestering agent being present in amounts sufficient to enhance the bleaching action of the perborate at the boil.

2. A composition as claimed in Claim 1 in which the copper salt is present in amount sufficient to provide from 30 to 300 parts of copper per million parts by weight of the detergent composition, and the sequestering agent is present in amount such that 3 to 15 molecules thereof are contained in the detergent composition per atom of copper.

3. A composition as claimed in Claim 1 in which the copper salt is present in amount sufficient to provide from 40 to 80 parts of copper per million parts by weight of the detergent composition, and the sequestering agent is present in amount such that 10 to 13 molecules thereof are contained in the detergent composition per atom of copper.

4. A composition as claimed in Claim 1 or Claim 2 or Claim 3 in which the detergent is a sodium salt of an alkyl aryl sulphonic acid.

5. A composition as claimed in Claim 4 in which the detergent is a sodium salt of an alkyl benzene sulphonic acid containing from 10 to 16 carbon atoms in the alkyl group.

6. A composition as claimed in any of the preceding claims in which the perborate is sodium perborate tetrahydrate.

7. A composition as claimed in any of the preceding claims in which the water-soluble copper salt is copper sulphate.

8. A composition as claimed in any of the preceding claims in which the sequestering agent is methylaminodiacetic acid or aminotriacetic acid or hydroxyethylaminodiacetic acid.

9. A composition as claimed in any of the preceding claims in which there are present, by weight, from 4 to 40% of the water-soluble organic anionic or non-ionic detergent, from 3 to 20% of the water-soluble perborate, from 40 to 90% of water-soluble inorganic salts and optionally up to 1% perfume and/or colouring matter and/or blueing agent.

10. A detergent composition as claimed in Claim 1 and substantially as described in any of Examples III to VIII.

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